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SALT EFFECTS IN PHOTOINDUCED ELECTRON TRANSFER
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G B SCHUSTER ET AL. 14 SEP 86 TR-41 N00014-86-K-0428

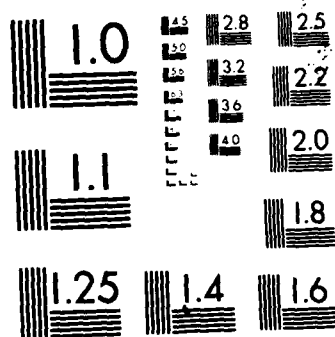
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SALT EFFECTS IN PHOTOINDUCED ELECTRON TRANSFER REACTIONS

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Summary: Metal salts and oxygen react synergistically to inhibit back-electron-transfer in photoinduced reactions.

The upsurge of interest in electron-transfer mediated photoreactions of organic compounds¹ has engendered new efforts to control the outcome of these processes. One of the more significant results is the discovery that added salts can greatly affect the products of these reactions. In one of the most striking examples of this phenomenon, Mizuno, Otsuji, and coworkers² recently reported that the photooxidation of several biphenyl derivatives is enhanced by the addition of $\text{Mg}(\text{ClO}_4)_2$. Other, perhaps related, effects of added salts have been reported by several other groups³ including our own.⁴ Herein we describe experiments that identify the root cause of some salt effects as the dramatic increase in the lifetime of free radical cations as a consequence of the inhibition of back electron transfer.

There are two distinct roles that salts might play in the enhancement of electron-transfer mediated photoreactions. The salt might increase the efficiency for formation of free radical ions after the initial electron transfer event. Or, the salt could act to increase the lifetime of the reactive radical ions after they are formed. These two possibilities can be easily distinguished with the laser techniques we have developed.⁵

The fluorescence of 1,4-dicyanonaphthalene (DCN) in acetonitrile solution is quenched by trans-stilbene (TS) or by 4,4'-dimethoxybiphenyl (DMB) at the diffusion limited rate. This is not a surprise since the Weller approach⁶ predicts that electron transfer in these examples will be exothermic by 12.9 and 17.8 kcal/mol respectively. Operation of the electron transfer scenario is confirmed with the observation of the expected radical ions by laser transient absorption spectroscopy. Figure 1 shows the absorption spectrum recorded ca. 500 ns after irradiation of DCN

in acetonitrile containing TS. The absorption with an apparent maximum at 390 nm is assigned to the dicyanonaphthalene radical anion (DCN^-)⁷ and that at 470 nm to the trans-stilbene radical cation (TS^+).⁸ When DMB is employed as the electron donor, its radical cation (DMB^+) is observed at 430 nm.⁹ The relative yields of these radical ions is readily estimated from their characteristic absorbances at early time in the experiment (<200 nsec) when their formation is complete, but no significant consumption has occurred.

The lifetimes of the DCN^- and TS^+ (or DMB^+) in the absence of an added trapping agent are apparently limited by back-electron-transfer. This is evidenced by the clean second-order reaction kinetics exhibited for consumption of these ions. A typical curve is shown on Figure 2, and the data are summarized in the Table.

Table: Relative Yields and Lifetimes of Radical Ions with Various Additives

Additives		ΔOD^a				$k_2/c(\text{cm/sec})^b$		
1	2	DCN^-	TS^+	DCN^-	DMB^+	DCN^-	TS^+	DMB^+
--	--	0.057	0.057	0.10	0.25	$(1.31 \pm 1.8) \times 10^6$	9.28×10^5	$(1.13 \pm 0.05) \times 10^6$
O_2	--	ND ^e	0.042	ND	0.16	ND	$(2.68 \pm 1.1) \times 10^5$	$(1.83 \pm 1.6) \times 10^4$
$\text{Mg}(\text{ClO}_4)_2$, .001 M	--	--	--	--	--	3.82×10^5	--	4.47×10^5
$\text{Mg}(\text{ClO}_4)_2$, .01 M	--	--	--	--	--	1.42×10^5	--	1.78×10^5
$\text{Mg}(\text{ClO}_4)_2$, .3 M	--	0.097	0.084	0.14	0.36	$(4.53 \pm 3.1) \times 10^4$	$(1.99 \pm .99) \times 10^5$	$(9.34 \pm .37) \times 10^4$
TBAClO_4^d	--	0.093	0.085	0.21	0.37	$(6.24 \pm 1.8) \times 10^5$	6.39×10^5	5.78×10^5
$\text{Mg}(\text{ClO}_4)_2$, .3 M	O_2	ND	0.066	ND	0.27	ND	$(2.92 \pm 1.1) \times 10^4$	$(2.42 \pm .74) \times 10^3$
TBAClO_4	O_2	ND	0.058	ND	0.13	ND	1.22×10^6	$(9.46 \pm .58) \times 10^5$

a) Change in absorbance at wavelength characteristic of the radical ion, proportional to its initial yield.

b) Bimolecular rate constant for consumption of the radical ion divided by the extinction coefficient of the ion (generally unknown) at the monitored wavelength. Values without standard deviations are from single measurements.

c) Solutions were saturated with O_2 by bubbling for 2 minutes.

d) 0.3 M tetra-n-butylammonium perchlorate.

e) Not detected because of the rapid quenching of DCN^- by O_2 .

Examination of the Table reveals three significant points concerning the influence of salts and oxygen as additives on the behavior of the radical ions. First, addition of the salt ($\text{Mg}(\text{ClO}_4)_2$ or TBAClO_4 ¹⁰) does not result in an increase in the yield of radical ions (compare ΔODs). Second, addition of $\text{Mg}(\text{ClO}_4)_2$, but not TBAClO_4 , causes the lifetime of TS^+ (or TMB^+) to increase ca. tenfold. Third, when the solution contains both O_2 and $\text{Mg}(\text{ClO}_4)_2$, the lifetime of TS^+ (or TMB^+) increases another 10-100 fold. These effects can be easily rationalized.

We propose that Mg^{+2} , but not TBA^+ , forms a complex with DCN^- that slows the rate of back electron transfer between DCN^- and TS^+ (or DMB^+). This, of course, increases the lifetime of the radical cation. The greatest increase in the radical cation lifetime is observed when both $\text{Mg}(\text{ClO}_4)_2$ and O_2 are present. We suggest that this is a consequence of two reactions: first,

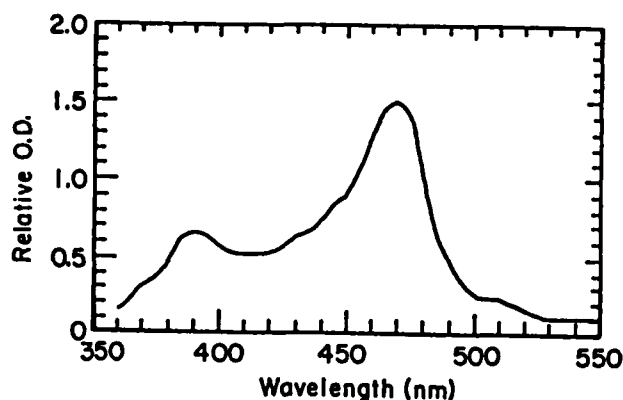


Figure 1. Transient absorption spectrum following laser flash photolysis of a system containing 1×10^{-5} M DCN and 2×10^{-2} M TS in CH_3CN .

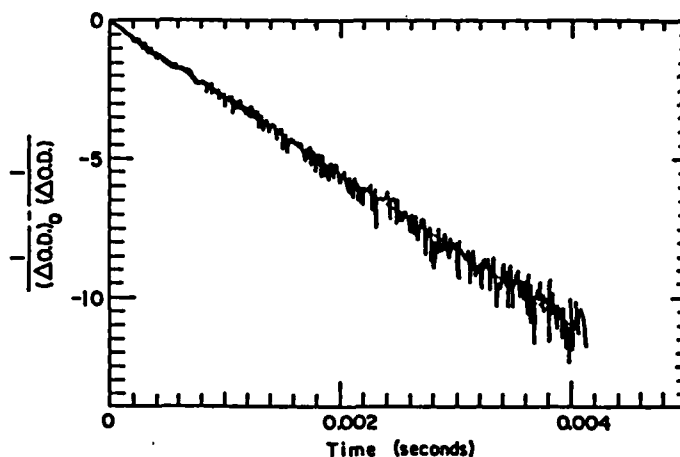


Figure 2. Plot of second-order fit of absorption decay of DMB^+ (generated by laser photolysis of an O_2 -saturated solution containing 1×10^{-5} M DCN, 2×10^{-2} M DMB, and 0.3 M $\text{Mg}(\text{ClO}_4)_2$ in acetonitrile).

electron transfer from DCN^- to O_2 to form $\text{O}_2^{\cdot-}$, and then complexation of Mg^{+2} with superoxide. The magnesium superoxide thus formed must be an especially ineffective electron donor to TS^+ (or DMB^+).

In summary, our data reveal that added salts do not significantly increase the yield of ions formed in photo-induced electron transfer reactions in polar (CH_3CN) solvent. The salt effect, and the synergistic O_2 effect,² operates through inhibition of back-electron-transfer. A related phenomenon has been reported for protic acids by Mattes and Farid.¹¹

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